Electron spin resonance in the S=1/2 quasi-one-dimensional antiferromagnet with Dzyaloshinskii-Moriya interaction $BaCu_2Ge_2O_7$

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We have investigated the electron spin resonance (ESR) on single crystals of $BaCu_2Ge_2O_7$ at temperatures between 300 and 2 K and in a large frequency band, 9.6 -134 GHz, in order to test the predictions of a recent theory, proposed by Oshikawa and Affleck (OA), which describes the ESR in a S=1/2 Heisenberg chain with the Dzyaloshinskii-Moriya interaction. We find, in particular, that the ESR linewidth, ΔH, displays a rich temperature behavior. As the temperature decreases from $T_{max}/2 \approx 170$ K to 50 K, ΔH shows a rapid and linear decrease, $\Delta H \sim T$. At low temperatures, below 50 K, ΔH acquires a strong dependence on the magnetic field orientation and for $H \| c$ it shows a $(h/T)^2$ behavior which is due to an induced staggered field h, according to OA's prediction.

While Bethe's solution [1] for a S=1/2 Heisenberg antiferromagnetic chain (1/2HAFC) has been known for more than 70 years, chain-like systems continue to attract considerable interest. One of the reasons is that the spin-singlet ground state of 1/2HAFC, in which quantum fluctuations manifest themselves in an extremely strong way as $T \to 0$, is unstable with respect to perturbations breaking the chain uniformity. This significantly affects the spin excitation spectrum in the low-energy sector, giving rise to a gapped state [2].

It appears that a uniform magnetic field, H, under certain conditions, also can induce a gap in the excitation spectrum of 1/2HAFC. While it is well established that the ground state of a 1/2HAFC in a magnetic field remains gapless provided that H does not exceed the saturation field, Dender et al.[3], performing neutron scattering experiments on the 1D antiferromagnetic chain-like compound Cu benzoate, have recently discovered that the magnetic field does create a gap in the spin excitations. They suggested that a staggered field h, arisen from the staggered g^s-tensor associated with the low local symmetry of the Cu^{2+} paramagnetic centers, is at the origin of this unexpected behavior. During the last years, these findings have generated a great deal of activity on a 1/2HAFC in a staggered field [4, 5, 6, 7].

The electron spin resonance (ESR) is a powerful tool for probing the low-energy magnetic excitations in solids with a unique sensitivity and resolution. However, a clear lack of a rigorous ESR theory, until very recently, has seriously retarded carrying out such experiments on 1/2HAFC . Notice that in conventional ESR theories the most important ingredient of the ESR physics, the dynamical four-spin correlation function, is evaluated within various decoupling schemes [8, 9]. Naturally, these kinds of approach fail in low-dimensional quantum spin systems where the many-body correlation effects are strong.

It was not until 1999 that Oshikawa and Affleck (OA) have developed an ESR theory for a 1/2HAFC based on a field theory approach [10, 11]. As the perturbations of 1/2HAFC, ensuring a nonzero linewidth, OA considered a staggered field h caused by the staggered g^s-tensor and the Dzyaloshinskii-Moriya (DM)interaction, $\Sigma \vec{D} \cdot \vec{S}_l \times \vec{S}_{l+1}$.They have shown that in a weak magnetic field, h can be approximated by $\vec{h} \approx g^s \vec{H} + \vec{D} \times g^u \vec{H}/2J$, J being an intrachain exchange [4]. Let us summarize briefly their main results as far as the ESR linewidth, ΔH, is concerned (for a more detailed discussion, see below). In the absence of h, the predictions of OA's theory are remarkably simple. The linewidth of the ESR signal in 1/2HAFC is linearly proportional to T for temperatures $T \ll J$, exhibiting a weak angular dependence on the direction of H. Now if 1/2HAFC is subjected to a staggered field h, the behavior of ΔH drastically changes: instead of having $\Delta H \sim T$ valid for $h = 0$, the width acquires a peculiar low-T dependence on h and T, $\Delta H \sim (h/T)^2$, diverging at low temperature. Experimentally, the magnitude of a staggered field can be controlled by a rotation of the applied magnetic field H. In the case where h is mainly due to the DM term, $h = 0$ if $H \| D$ and $h = h_{max}$ for $H \perp D$, as it is easily seen from the above expression for $\vec{h}$. Since $h \sim H$, this should lead to a strong dependence of ΔH on the H direction. Finally, at very low temperature, $T \ll H$, the ESR spectrum is dominated by soliton-like excitations [10].

Some of these theoretical results have already received support through ESR experiments on Cu benzoate. In particular, the very low-T regime has been studied in detail in several works [12, 13]. There remain, however, interesting open problems related to the low-T and intermediate-T spin dynamics of 1/2HAFC. To date, to the best of our knowledge, there has been no convincing evidence confirming the T-linear dependence of ΔH in a 1/2HAFC at intermediate temperatures. As far as

the low-T $(h/T)^2$- contribution to ΔH is concerned, although the ESR data on Cu benzoate are found to be in good qualitative agreement with the theoretical predictions, a quantitative comparison between the theory and the experiment is still lacking. Even more importantly, the only material which has been studied, up to now, for the purpose of testing the OA ESR theory is Cu benzoate. Clearly, new model 1/2HAFC systems are necessary in order to carry out a comprehensive test of the theoretical predictions. In this Letter all of these points are addressed by performing an extensive ESR study in a wide frequency and temperature range on a new $S = 1/2$ chain-like antiferromagnet with DM interaction, $BaCu_2Ge_2O_7$. Our results provide new evidence in favor of the OA theory.

The crystal structure of $BaCu_2Ge_2O_7$,which belongs to the orthorhombic space group $Pnma$ ($Z = 4$), is made of zigzag chains of corner-sharing CuO_4 plaquettes running along the crystallographic c axis (Fig. 1a) (for a detailed description of the crystal structure, see Ref. [14]). The Cu-O-Cu bond angle is found to be 135°. This is much smaller than the 180°-angle that occurs in superexchange bridges of many 2D cuprates. This implies that the staggered g^s-tensor and the DM interaction are present in the spin Hamiltonian of an individual CuO_3 chain. The magnetic properties of $BaCu_2Ge_2O_7$ are known from the neutron-diffraction, magnetic susceptibility, $\chi(T)$, and magnetization measurements [14, 15]. From the low-T part of $\chi(T)$ measured below 350 K, the intrachain exchange integral $J \approx 540$ K has been extracted by comparison with the Bonner-Fisher curve for a 1/2HAFC. Interchain interactions in $BaCu_2Ge_2O_7$ lead to an antiferromagnetic long-range order at low T, $T_N = 8.8$ K, with spins aligned parallel to an easy c-axis and a weak ferromagnetic moment along b-axis as established in the magnetization measurements [15]. Thus this compound, with a ratio $T_N/J = 0.017$, can be viewed as a nearly ideal model system for a 1/2HAFC with the DM interaction.

The single crystals of $BaCu_2Ge_2O_7$ used in the ESR experiments were grown by a floating-zone method. Particular attention was paid to the crystal orientation, since the a- and c-axis lengths are almost the same. The ESR spectra in X-band ($\nu = 9.6$ GHz) and Q-band ($\nu = 34$ GHz) were collected using a Bruker EMX spectrometer. At high frequencies, a homemade millimeter-range video spectrometer has been used.

In order to minimize the effect of the $(h/T)^2$-contribution to $\Delta H(T)$ which can be important at low T, the ESR at the lowest frequency (lowest resonance magnetic field) was performed first. A broad single ESR line was characterized by the following ESR parameters at room temperature: $\Delta H_a = 0.2650 \pm 0.0002$ T, $\Delta H_b = 0.1990 \pm 0.0002$ T, $\Delta H_c = 0.1740 \pm 0.0002$ T and $g_a = 2.22 \pm 0.001$, $g_b = 2.08 \pm 0.001$, $g_c = 2.09 \pm 0.001$, where the subscripts a, b, c indicate the magnetic field direction.

The temperature dependence of the linewidth in $BaCu_2Ge_2O_7$ for magnetic field orientation along the three principal axes at $\nu = 9.6$ GHz is shown in Fig. 1b. For comparison $\Delta H(T)$ data for $KCuF_3$, to date the most studied 1/2HAFC-like material, from Ref. [16], are also presented. Please note that normalized coordinates are used both for ΔH and the temperature (the latter is normalized by $T_{max} \approx 0.64J$, the temperature corresponding to the maximum of the static susceptibility). The values of $T_{max} = 346$ K and $T_{max} = 243$ K were taken for $BaCu_2Ge_2O_7$ and for $KCuF_3$, respectively. ΔH is normalized by its value at $T = T_{max}/2$. As is clearly seen from this figure, when T decreases and approaches $\sim T_{max}/2$, the slope of $\Delta H(T)$ changes, displaying a crossover from the "classical" Kubo-Tomita regime to the predicted quantum one. At this temperature the correlation length along the chains $\xi/a \approx 2$ (where a is the distance between nearest Cu sites in the chain direction). This quite naturally establishes the limits of the validity of the field theory approach. Below $T_{max}/2$, the linewidth, indeed, follows the linear dependence $\Delta H \sim T$ in a large T-interval, as predicted by OA's theory (see Ref. [17] for alternative models) .

At low T another contribution to ΔH, which we call ΔH_{3D}, becomes important. Since ΔH_{3D} contributes to ΔH at temperatures close to T_N we tentatively interpret it as due to the 3D Néel phase fluctuations. As T decreases, ΔH_{3D} first increases and then shows a tendency to decrease. We have tried to fit $\Delta H(T)$ for $H \| c$ using the equation $\Delta H(T) \sim A \cdot T + \Delta H_{3D}(T)$, where a diverging part of ΔH_{3D} is represented by $\Delta H_{3D}(T) = B \cdot (T - T_N)^n$, in order to have an estimate for n. The fit, shown in Fig. 1b by the solid line, gives $n = -1.1$. Thus, ΔH_{3D}, can not be identified with the $(h/T)^2$-contribution and, in fact, as we show below, is found not to depend on the magnetic field.

Let us now turn to our results of high-frequency ESR experiments on $BaCu_2Ge_2O_7$. In what follows we shall compare systematically the ESR data for two field orientations, $H \| a$ and $H \| c$. Fig. 2a shows the linewidth, as a function of temperature below 70 K for $H \| a$, measured at frequencies 9.6, 34 and 134 GHz. Note that in this T interval the above discussed $\Delta H_{3D}(T)$ contribution is of main importance. Despite the fact that the operating frequency is changed almost by a factor of 15, $\Delta H(T)$ remains unchanged within experimental accuracy. Therefore it is reasonable to assume that the sum of the linear and ΔH_{3D} contribution is frequency independent. In Fig. 2b we have plotted $\Delta H(T)$ for $H \| c$ as the difference between $\Delta H(T, \nu)$ measured at the frequency ν ($\nu =$ 34, 70.6 and 134 GHz) and $\Delta H(T, 9.6$ GHz) measured at $\nu = 9.6$ GHz. (Notice that the maximum value of $\Delta H(T, 9.6$ GHz) at low-T, i.e. the value that is subtracted from the shown curves, is less than 0.13 T.) The ESR data for the magnetic field direction $H \| c$ is found to

be in significant contrast with those of $H\|a$. As evident from Fig. 2b, $\Delta H(T,\nu)$ strongly depends on both the temperature and the frequency (or the resonance field). According to OA's theory this is a staggered field, h, induced by an applied uniform magnetic field H which is responsible for these phenomena. Therefore, to compare the obtained results with the theory one needs more information about h. To this end we have undertaken antiferromagnetic resonance (AFMR) studies on $BaCu_2Ge_2O_7$ below T_N. The idea to use the AFMR for the staggered field determination resides in the fact that, for H applied along the principal crystal axes, among the two resonance modes there exists one, called "antiferromagnetic mode", which depends strongly on h, $\nu \sim \sqrt{h}$ and another one, usually called "ferromagnetic" mode, which depends mostly on H, $\nu \sim H$ [22].

Experimentally, two modes of antiferromagnetic resonance have been found in $BaCu_2Ge_2O_7$ at 2 K. The corresponding frequencies at $H = 0$, $\nu_1(0) = 22$ GHz and $\nu_2(0) = 56$ GHz. What we need in order to proceed in our discussion of the staggered field in $BaCu_2Ge_2O_7$ is the magnetic field dependence of ν_2 for $H\|c$ and that of ν_1 for $H\|a$. In Fig. 3 $\nu_2(H)$ for $H\|c$ measured at $T = 2$ K is shown. The solid line follows the equation $(\nu_2/\gamma)^2 = (\nu_{20}/\gamma)^2 + 4SJh$ which results from the spin-wave theory for a 1/2HAFC, where the staggered field is given by $h = C \cdot H$ (see, for example, [7]). The best fit gives a product $4SJ \cdot C = 18.7 \pm 0.15$ T. Since S is strongly reduced by the zero-point fluctuations, to get C, an estimate of the mean field value of S, $\overline{S}$, is now required. This can be done by means of a recent theory by Irkhin and Katanin [23]. Inserting the values of $J = 540$ K and $T_N = 8.8$ K in their eq.(21), one obtains $\overline{S} = 0.088$ which leads to $C = 0.14$ for $H\|c$. As far as the field dependence of ν_1 for $H\|a$ is concerned we have found that $\nu_1(H)$ varies only slightly with H. Nevertheless, $4SJ \cdot C$ can be estimated in this case as 1.2 ± 0.25T leading to $C = 0.0074$. [Note, however, that an imperfect magnetic field orientation could also be at the origin of this small variation of $\nu_1(H)$.] Thus, our important conclusion, which is due to the high frequency AFMR measurements, is that the magnitude of h induced by the applied magnetic field H strongly depends on the direction of H, taking a maximum value for $H\|c$. This is consistent with the ESR linewidth data presented in Fig. 2 : ΔH is frequency independent for $H\|a$ and it exhibits a rather strong frequency (magnetic field) dependence for $H\|c$.

We are now at a point to make a quantitative comparison between our results and those of OA's theory. Their prediction for the temperature and magnetic field linewidth dependence at low T is $\Delta H \approx 0.69(\ln J/T)Jh^2/T^2$. This equation, with the logarithmic factor replaced by unity, was already used to describe the ESR data on copper benzoate [10, 11]. Therefore we try first to fit our data in Fig. 2b making the same assumption. The best fit giving $C = 0.16$ is shown in Fig. 2b by the solid lines. Comparing this with our estimate from the AFMR experiment, $C = 0.14$, one can conclude that the OA equation, taken with $\ln(J/T) \approx 1$, slightly underestimates ΔH, by approximately 15%, but that it captures the essential of the spin dynamics of 1/2HAFC in a staggered field at a quantitative level. Let us now test the above equation in its complete form (i.e. including the log correction). As it can be seen from Fig. 2b, where the theoretical curves are presented by the dashed lines, again the equation fits well to the experimental data giving $C = 0.09$, which is about 35% less than the experimental value. Since there are no adjustable parameters in the theory, other than C, one should consider the theory to be in excellent agreement with the experiment.

In conclusion, we have undertaken detailed ESR measurements on the new S=1/2 quasi-one dimensional compound with Dzyaloshinskii-Moriya interaction, $BaCu_2Ge_2O_7$. We have essentially focused on the temperature and frequency behavior of the linewidth in two distinct T-intervals. At intermediate T, in accordance with the OA theory, the linewidth is found to be linearly proportional to the temperature and frequency independent, regardless of the field orientation. The crossover from the Kubo-Tomita behavior to the T-linear regime takes place at around $T_{max}/2$. This establishes the high-T limit of the validity of the field theory approach. At low temperatures ($T_N < T \ll T_{max}/2$) the linewidth behavior strongly depends on the magnetic field orientation. For $H\|c$, corresponding to the maximum of the staggered field h induced in the system, the linewidth scales approximately as $(h/T)^2$ in agreement with the theory. To infer the key theory parameter, the proportionality constant C, from an independent experiment, we have carried out AFMR measurements at $T < T_N$. We were able then, for the first time, to perform a detailed quantitative comparison between our results and the theoretical predictions.

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[17] Various models were proposed in order to explain the linear-T dependence of ΔH, $\Delta H(T) = \alpha + \beta T$. These are based either on the spin diffusion concept [18], the spin-phonon coupling mechanism [19] or the considering of the effect of static spin correlations on the linewidth [20]. However, all of these models are valid at relatively high temperatures, $T > J$, as compared with the T interval which is of interest in the present study. Besides, note that the latter model suffers from an improper evaluation of the second moment in the case of the 1/2HAFC with the DM interaction [11, 21].
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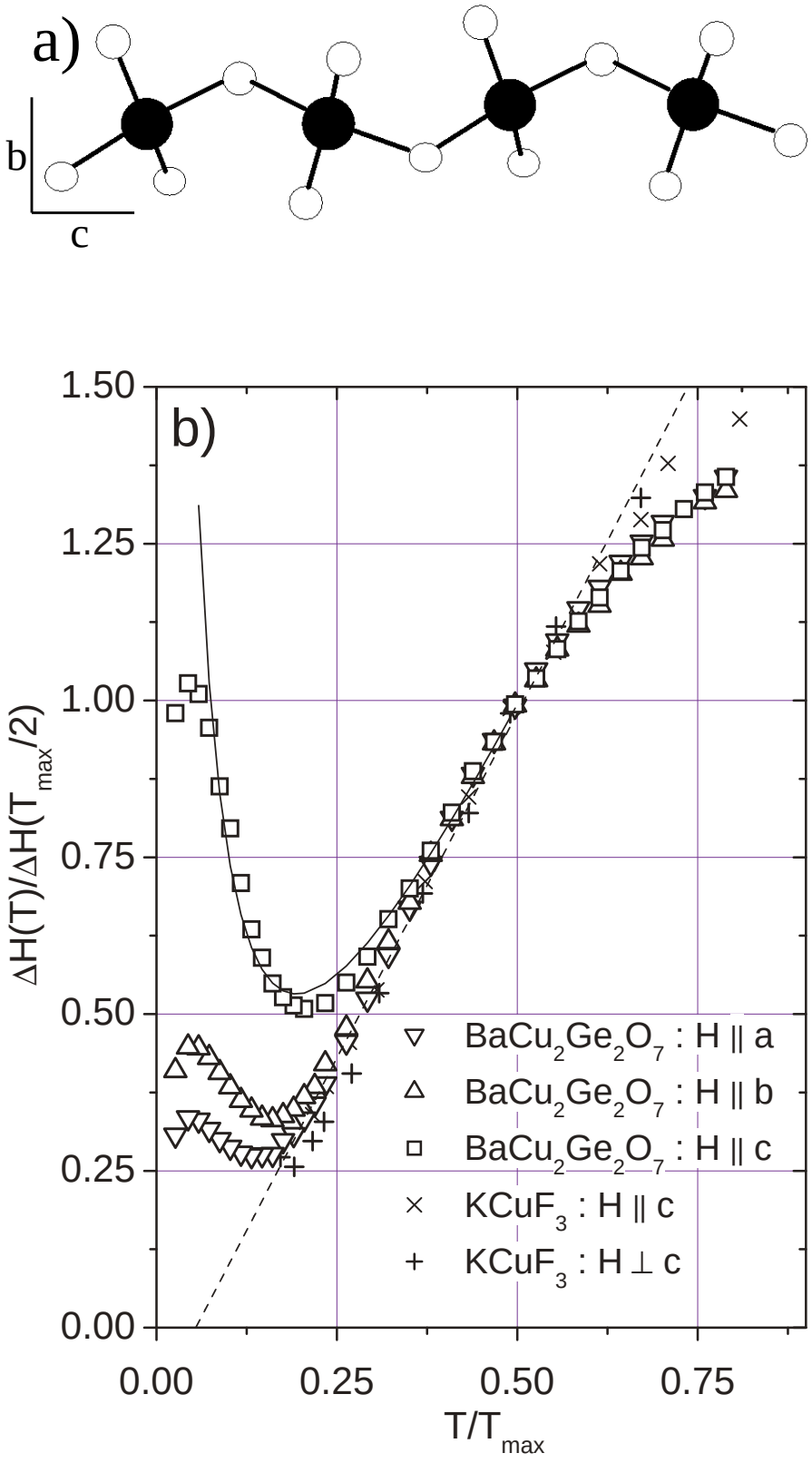

FIG. 1: (a) The (b,c)-plan projection of a fragment of the zigzag chain of corner-sharing CuO_4 plaquettes. The black circles are Cu^{2+} ions, the open circles are O^{2-}; (b) The temperature dependence of the linewidth in $BaCu_2Ge_2O_7$ along the three principal crystallographic directions, at ν =9.6 GHz, presented in normalized coordinates (see text). Data for $KCuF_3$ from Ref. [16] are also shown. The solid line results from the fit, the dashed line is a guide to the eye.

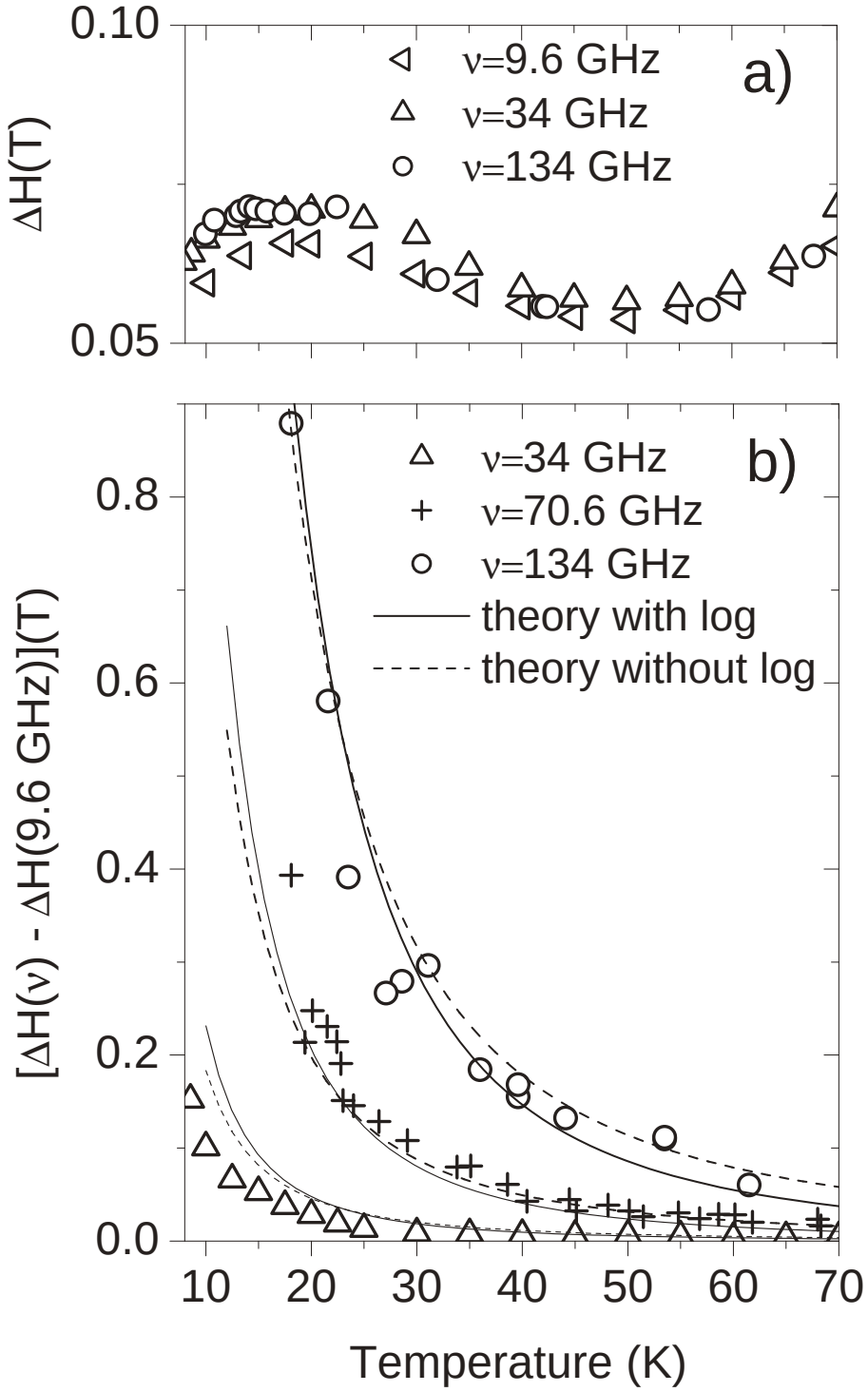

FIG. 2: a) $\Delta H(T)$ for $H \| a$ as a function of frequency; b) The temperature dependence of the difference between $\Delta H(T,\nu)$ measured at a frequency ν and $\Delta H(T, 9.6\text{ GHz})$ measured at $\nu = 9.6$ GHz, for $H \| c$ in $BaCu_2Ge_2O_7$. The solid and the dashed lines are according to Eq. (9) of Ref. [10].

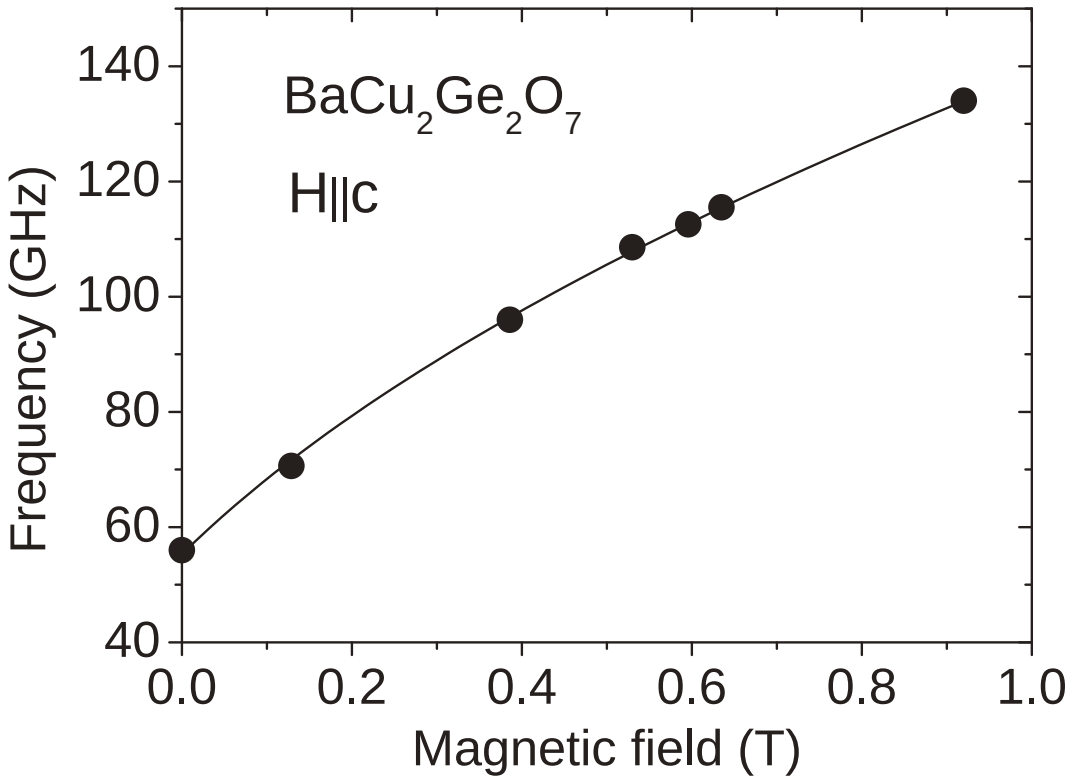

FIG. 3: The frequency-vs-field diagram of the AFMR mode $\nu_2(H)$ in $BaCu_2Ge_2O_7$ at $T = 2$K, for $H \| c$.